

# Improvement of ${}^4I_{11/2} \rightarrow {}^4I_{13/2}$ Transition Rate and Thermal Stabilities in $\text{Er}^{3+}$ -Doped $\text{TeO}_2\text{-B}_2\text{O}_3$ ( $\text{GeO}_2$ )- $\text{ZnO-K}_2\text{O}$ Glasses

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Spectroscopic and thermal analysis indicates that tellurite glasses doped with  $\text{B}_2\text{O}_3$  and  $\text{GeO}_2$  are promising candidate host materials for wide-band erbium doped fiber amplifier (EDFA) with a high 980 nm pump efficiency. In this study, we measured the thermal stabilities and the emission cross-sections for  $\text{Er}^{3+}$ :  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  transition in this tellurite glass system. We also determined the Judd-Ofelt parameters and calculated the radiative transition rates and the multiphonon relaxation rates in this glass system. The 15 mol% substitution of  $\text{B}_2\text{O}_3$  for  $\text{TeO}_2$  in the  $\text{Er}^{3+}$ -doped  $75\text{TeO}_2\text{-}20\text{ZnO-}5\text{K}_2\text{O}$  glass raised the multiphonon relaxation rate for  ${}^4I_{11/2} \rightarrow {}^4I_{13/2}$  transition from  $4960 \text{ s}^{-1}$  to  $24700 \text{ s}^{-1}$ , but shortened the lifetime of the  ${}^4I_{13/2}$  level by 14 % and reduced the emission cross-section for the  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  transition by 11%. The 15 mol%  $\text{GeO}_2$  substitution in the same glass system also reduced the emission cross-section but increased the lifetime by 7%. However, the multiphonon relaxation rate for  ${}^4I_{11/2} \rightarrow {}^4I_{13/2}$  transition was raised merely by  $1000 \text{ s}^{-1}$ . Therefore, a mixed substitution of  $\text{B}_2\text{O}_3$  and  $\text{GeO}_2$  for  $\text{TeO}_2$  was concluded to be suitable for the 980 nm pump efficiency and the fluorescence efficiency of  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  transition in  $\text{Er}^{3+}$ -doped tellurite glasses.

## I. INTRODUCTION

A tellurite-based erbium doped fiber amplifier (T-EDFA) provides a wide amplifying bandwidth due to its high stimulated emission cross-section [1], [2]. T-EDFA shows a broad bandwidth of over 70 nm with a medium population inversion in contrast to a silica-based EDFA that shows about a 30 nm bandwidth. The EDFA for amplification of 1.5  $\mu\text{m}$  signal can use both 980 nm and 1480 nm optical pumping. Generally, the 1480 nm pumping is suitable for high power EDFA because the ground state absorption to  ${}^4I_{13/2}$  manifold has a high absorption cross-section relative to that of  ${}^4I_{11/2}$ . However, the 1480 nm pumping is a resonant pumping scheme that cannot provide full population inversion and good signal-to-noise ratio (S/N)[3]. Thus, the 980 nm pumping scheme on T-EDFA is necessary for the wide bandwidth optical amplifier with a good noise figure. It has been reported that the small signal gain of T-EDFA with 980 nm pumping is significantly lower than that with 1480 nm pumping [4]. This may be due to the low phonon energy of tellurite glasses. For  $\text{Er}^{3+}$  doped in silicate glasses, the lifetime of  ${}^4I_{11/2}$  is less than 10  $\mu\text{s}$  due to the high multiphonon relaxation rate, and population feeding from  ${}^4I_{11/2}$  to  ${}^4I_{13/2}$  results dominantly from the multiphonon relaxation [5]. The highest phonon energy of silicate glasses is around  $1100 \text{ cm}^{-1}$ , while that of tellurite glasses is around  $700 \text{ cm}^{-1}$  [6]. Therefore, the multiphonon relaxation rate of the  ${}^4I_{11/2} \rightarrow {}^4I_{13/2}$  transition of  $\text{Er}^{3+}$  in tellurite glasses is much smaller than that in silicate glasses, and the lifetime of  ${}^4I_{11/2}$  for tellurite glasses is much longer than that for silicate glasses. This results in several undesirable effects on the 980 nm pumping efficiency in  $\text{Er}^{3+}$ -doped tellurite glasses. First, the accumulation of population in the

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$^4I_{13/2}$  level becomes difficult because the branching ratio of the radiative  $^4I_{11/2} \rightarrow ^4I_{13/2}$  transition is about four times smaller than that of the  $^4I_{11/2} \rightarrow ^4I_{15/2}$  transition [7]. Secondly, the cross relaxation of  $^4I_{11/2} : ^4I_{11/2} \rightarrow ^4F_{7/2} : ^4I_{15/2}$  may depopulate the  $^4I_{11/2}$  level. Finally, excited state absorption of  $^4I_{11/2} \rightarrow ^4F_{7/2}$  by the pumping light can also depopulate the  $^4I_{11/2}$  level [8]. Consequently, the improvement in the multiphonon relaxation rate of  $^4I_{11/2} \rightarrow ^4I_{13/2}$  in  $Er^{3+}$ -doped tellurite glasses can enhance the population accumulation in the  $^4I_{13/2}$  level and the 980 nm pumping efficiency. We have already proposed that the  $Ce^{3+}$ -codoping can enhance the 980 nm pumping efficiency through the non-radiative energy transfer  $Er^{3+} : ^4I_{11/2}, Ce^{3+} : ^2F_{5/2} \rightarrow Er^{3+} : ^4I_{13/2}, Ce^{3+} : ^2F_{7/2}$  [9]. In this study, we propose another effective method to increase the 980 nm pumping efficiency. The addition of  $B_2O_3$  along with  $GeO_2$  into  $Er^{3+}$ -doped tellurite glasses is considered to increase the highest phonon energy of host glasses and the multiphonon relaxation rate of the  $^4I_{11/2} \rightarrow ^4I_{13/2}$  transition, and then successfully to enhance the population accumulation in the  $^4I_{13/2}$  level and the 980 nm pumping efficiency.

## II. EXPERIMENTAL

Glass samples were prepared by a conventional melting and quenching method. Starting materials were oxide and carbonate powders with more than 99.9% purity. Melting was carried out in air by using an electric furnace. Mixed powder was melted in an alumina crucible at 950°C for 60 minutes, and cast on a brass plate preheated at about 200°C, then annealed at 380°C for 20 minutes. Glass transition and crystallization temperatures were measured by differential scanning calorimetry (DSC) thermal analysis. A Ti: sapphire laser excited by Ar ion laser was used to pump the sample, and a monochromator and an InGaAs detector were used to measure the fluorescence spectrum. The fluorescence lifetimes for the  $^4I_{11/2}$  and  $^4I_{13/2}$  levels were measured with a Ti: sapphire laser, a chopper wheel, and the optical detector coupled with a HP 500 MHz digital oscilloscope. The wavelength of the excitation laser was tuned to 800 nm for the fluorescence spectrum and lifetime measurements. Absorption spectra were measured with a UV-Visible-NIR spectrophotometer.

## III. RESULTS AND DISCUSSION

All the  $Er^{3+}$ -doped glass samples were of transparently pink color. DSC curves of  $75TeO_2-20ZnO-5K_2O$ ,  $60TeO_2-15BO_{3/2}-20ZnO-5K_2O$ , and  $60TeO_2-7.5BO_{3/2}-7.5GeO_2-20ZnO-5K_2O$  glasses are shown in Fig. 1. Crystallization on-set temperature,  $T_x$ , and crystallization peak temperature,  $T_c$ , were significantly

increased, and glass transition temperature,  $T_g$ , was decreased with substitution of  $B_2O_3$  and  $GeO_2$  for  $TeO_2$ . Table 1 shows the changes of  $T_g$ ,  $T_x$ ,  $T_c$  and  $T_x - T_g$  with the concentration of  $B_2O_3$  and  $GeO_2$ . The value of  $T_x - T_g$  has been frequently used as a measure of thermal stability of the host glass for fiber drawing [10], [11]. It is desirable for a host glass to have a large value of  $T_x - T_g$  for an optical fiber drawing. As shown in Table 1, the value of  $T_x - T_g$  was increased with substitutions of  $B_2O_3$  or  $GeO_2$  for  $TeO_2$ , and increased further with mixed substitutions of  $B_2O_3$  and  $GeO_2$  compared to the separate  $B_2O_3$  or  $GeO_2$  substitutions. Thermal stability of tellurite glasses may be improved with the addition of  $SiO_2$ , but  $SiO_2$  cannot use for substitution material because  $TeO_2-SiO_2-ZnO-K_2O$  glasses were spontaneously phase separated even though glass melt was quenched by a brass plate. Since  $B_2O_3$  and  $GeO_2$  are glass network formers having a high phonon energy, their additions into tellurite glasses can improve the glass forming ability and thus enhance the thermal stability.

Emission spectra of  $75TeO_2-20ZnO-5K_2O-0.1Er_2O_3$ ,  $60TeO_2-15GeO_2-20ZnO-5K_2O-0.1Er_2O_3$ , and  $60TeO_2-15BO_{3/2}-$

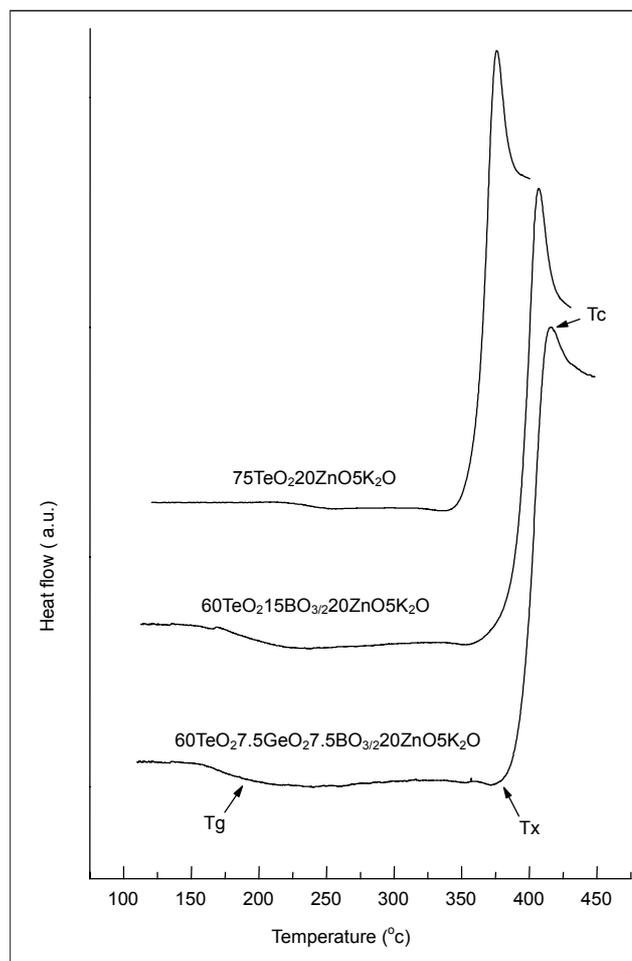


Fig. 1. DSC curves for tellurite glasses.

Table 1.  $T_g$ ,  $T_x$  and  $T_x-T_g$  of tellurite glasses measured by DSC.

Composition	$T_g$ (°C)	$T_x$ (°C)	$T_c$ (°C)	$T_x-T_g$
75TeO <sub>2</sub> -20ZnO-5K <sub>2</sub> O	235±5	342±2	376±2	107
70TeO <sub>2</sub> -5BO <sub>3/2</sub> -20ZnO-5K <sub>2</sub> O	205±7	355±2	384±2	150
65TeO <sub>2</sub> -10BO <sub>3/2</sub> -20ZnO-5K <sub>2</sub> O	200±5	360±3	392±3	160
60TeO <sub>2</sub> -15BO <sub>3/2</sub> -20ZnO-5K <sub>2</sub> O	200±5	360±2	392±2	160
60TeO <sub>2</sub> -15GeO <sub>2</sub> -20ZnO-5K <sub>2</sub> O	220±5	373±2	404±2	153
60TeO <sub>2</sub> -12GeO <sub>2</sub> -3BO <sub>3/2</sub> -20ZnO-5K <sub>2</sub> O	210±7	373±3	404±3	163
60TeO <sub>2</sub> -7.5GeO <sub>2</sub> -7.5BO <sub>3/2</sub> -20ZnO-5K <sub>2</sub> O	200±5	378±2	409±2	178

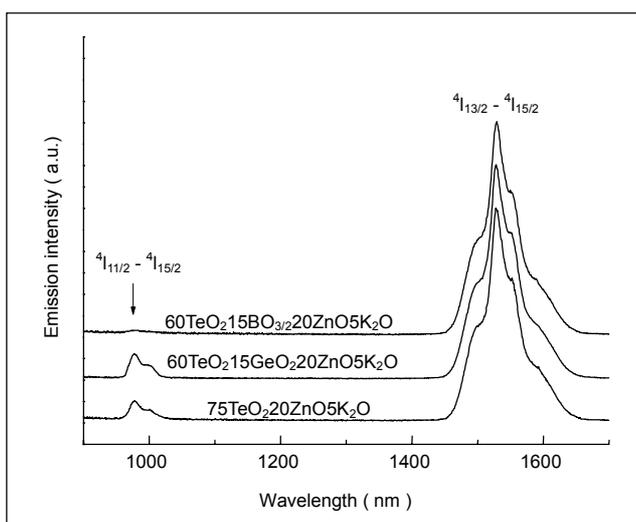


Fig. 2. Emission spectra for Er<sup>3+</sup>-doped tellurite glasses.

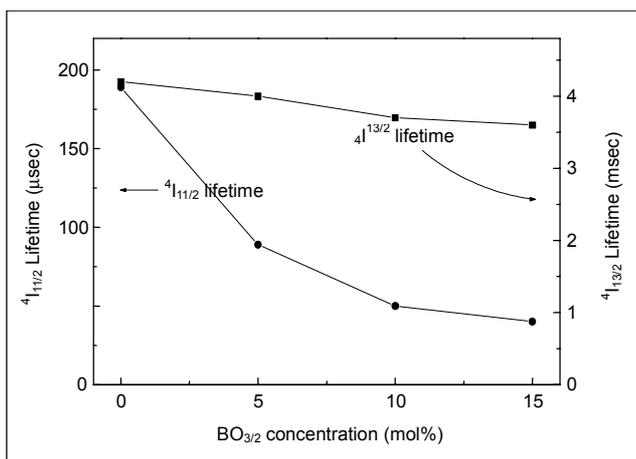


Fig. 3. The dependence of <sup>4</sup>I<sub>11/2</sub> and <sup>4</sup>I<sub>13/2</sub> lifetimes on B<sub>2</sub>O<sub>3</sub> concentrations in (75-x) TeO<sub>2</sub>-xBO<sub>3/2</sub>-20ZnO-5K<sub>2</sub>O glasses.

20ZnO-5K<sub>2</sub>O-0.1Er<sub>2</sub>O<sub>3</sub> glasses are shown in Fig. 2. The GeO<sub>2</sub> substitution for TeO<sub>2</sub> hardly changed the shape of emission spectrum of Er<sup>3+</sup>, but the B<sub>2</sub>O<sub>3</sub> substitution almost elimi-

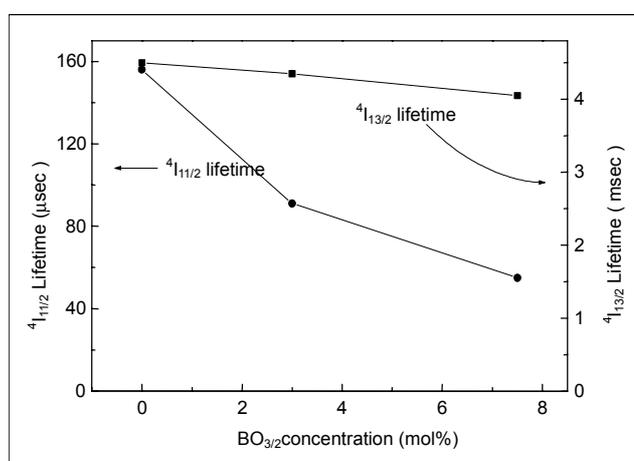


Fig. 4. The dependence of <sup>4</sup>I<sub>11/2</sub> and <sup>4</sup>I<sub>13/2</sub> lifetimes on B<sub>2</sub>O<sub>3</sub> concentrations in 60TeO<sub>2</sub>-(15-x) GeO<sub>2</sub>-xBO<sub>3/2</sub>-20ZnO-5K<sub>2</sub>O glasses.

nated the 980 nm emission (<sup>4</sup>I<sub>11/2</sub> → <sup>4</sup>I<sub>15/2</sub>) peak. The B<sub>2</sub>O<sub>3</sub> substitution was more effective than the GeO<sub>2</sub> substitution for optical quenching of <sup>4</sup>I<sub>11/2</sub> → <sup>4</sup>I<sub>15/2</sub> transition. Figure 3 shows the lifetime dependence of the <sup>4</sup>I<sub>11/2</sub> and <sup>4</sup>I<sub>13/2</sub> levels on the B<sub>2</sub>O<sub>3</sub> concentration in (75-x)TeO<sub>2</sub>-xBO<sub>3/2</sub>-20ZnO-5K<sub>2</sub>O glasses. The lifetime of the <sup>4</sup>I<sub>11/2</sub> level was remarkably shortened as the B<sub>2</sub>O<sub>3</sub> concentration increased, while that of <sup>4</sup>I<sub>13/2</sub> showed a small change. Figure 4 shows the lifetime dependence of the <sup>4</sup>I<sub>11/2</sub> and <sup>4</sup>I<sub>13/2</sub> levels on the B<sub>2</sub>O<sub>3</sub> concentration in 60TeO<sub>2</sub>-(15-x)GeO<sub>2</sub>-xBO<sub>3/2</sub>-20ZnO-5K<sub>2</sub>O glasses. As shown in Fig. 3 and 4, the lifetimes for <sup>4</sup>I<sub>11/2</sub> and <sup>4</sup>I<sub>13/2</sub> of Er<sup>3+</sup> in a 75TeO<sub>2</sub>-20ZnO-5K<sub>2</sub>O glass were measured to be 190 μs and 4.2 ms, respectively. Those in a 60TeO<sub>2</sub>-15GeO<sub>2</sub>-20ZnO-5K<sub>2</sub>O glass were 160 μs and 4.5 ms, and those in a 60TeO<sub>2</sub>-15BO<sub>3/2</sub>-20ZnO-5K<sub>2</sub>O glass were 40 μs and 3.6 ms, respectively. The decreasing effect on the lifetime for <sup>4</sup>I<sub>11/2</sub> level by the GeO<sub>2</sub> substitution was much smaller than that by the B<sub>2</sub>O<sub>3</sub> substitution. The substitution of GeO<sub>2</sub> for TeO<sub>2</sub> increased the lifetime of the <sup>4</sup>I<sub>13/2</sub> level, but the substitution of B<sub>2</sub>O<sub>3</sub> for TeO<sub>2</sub> shortened it.

Table 2. Refractive indices and Judd-Ofelt intensity parameters of Er<sup>3+</sup> in tellurite glasses.

Composition	n (1500 nm)	Ω <sub>2</sub> (10 <sup>-20</sup> cm <sup>2</sup> )	Ω <sub>4</sub> (10 <sup>-20</sup> cm <sup>2</sup> )	Ω <sub>6</sub> (10 <sup>-20</sup> cm <sup>2</sup> )	rms (%)
75TeO <sub>2</sub> -20ZnO-5K <sub>2</sub> O	2.06	5.95	2.06	1.07	3.2
60TeO <sub>2</sub> -15BO <sub>3/2</sub> -20ZnO-5K <sub>2</sub> O	1.97	7.33	2.60	1.19	2.9
60TeO <sub>2</sub> -15GeO <sub>2</sub> -20ZnO-5K <sub>2</sub> O	2.00	6.98	2.52	1.10	4.2
60TeO <sub>2</sub> -7.5GeO <sub>2</sub> -7.5BO <sub>3/2</sub> -20ZnO-5K <sub>2</sub> O	1.98	7.15	2.60	1.19	2.9

Measured decay rate ( $W_m$ ) from the excited state energy level can be expressed as

$$W_m = W_r + W_{mp} + W_{et} + W_{cr}, \quad (1)$$

where  $W_r$  is the radiative transition rate calculated from Judd-Ofelt analysis and  $W_{mp}$ ,  $W_{et}$  and  $W_{cr}$  are the rates of non-radiative transitions due to multiphonon relaxation, energy transfer, and cross relaxation, respectively [12]. Because the concentration of the Er<sup>3+</sup> ion was kept low enough,  $W_{et}$  and  $W_{cr}$  can be neglected in our cases. Thus,  $W_m$  can be written as

$$W_m = \frac{1}{\tau_m} = W_r + W_{mp}. \quad (2)$$

The Judd-Ofelt (J-O) approach for determining radiative and nonradiative transition rates of rare earth ion in glass has been widely used [7], [10], [13]. In the J-O analysis, the line strength for an electric dipole transition is given by

$$S_{ed}(aJ; bJ') = e^2 \sum_{t=2,4,6} \Omega_t \left\langle f^N [\alpha SL] J \left| U^{(t)} \right| f^N [\alpha' S' L' ] J' \right\rangle^2, \quad (3)$$

where  $\Omega_t$  is J-O parameter and  $\langle U^{(t)} \rangle$  is doubly reduced matrix element [14], [15]. The J-O parameters are determined from absorption spectra and refractive indices. We calculated the values of  $\Omega_2$ ,  $\Omega_4$ , and  $\Omega_6$  for our tellurite glass samples by using the procedure provided in [13]. In these calculations, the doubly reduced matrix elements from Weber [16] were used. The values of J-O parameters for the tellurite glasses are listed in Table 2. After obtaining J-O parameters, the radiative transition rate ( $W_r$ ) can be determined by

$$W_r(aJ; bJ') = \frac{16\pi^3 n^2}{3h\epsilon_0 \lambda^3 (2J+1)} (\chi_{ed} S_{ed} + \chi_{md} S_{md}), \quad (4)$$

where the  $\chi$  terms account for a local field correction and are

given by  $\chi_{ed} = (n^2+2)^2/9n$  and  $\chi_{md} = n$  [16], [17]. By using (2) and (4), the multiphonon relaxation rates can be determined. The calculated radiative transition rates ( $W_r$ ), measured lifetimes ( $\tau_m$ ), quantum efficiencies ( $\eta = \tau_m/\tau_r$ ), and multiphonon relaxation rates ( $W_{mp}$ ) of Er<sup>3+</sup> in the tellurite glasses are listed in Table 3. It can be seen from Table 3 that the  $W_{mp}$  for <sup>4</sup>I<sub>11/2</sub> → <sup>4</sup>I<sub>13/2</sub> transition was increased significantly by the B<sub>2</sub>O<sub>3</sub> substitution; however, the change of that by the GeO<sub>2</sub> substitution was small. The calculations for  $W_{mp}$  of <sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub> transitions resulted in nearly 0 in the tellurite glasses except for 60TeO<sub>2</sub>-15BO<sub>3/2</sub>-20ZnO-5K<sub>2</sub>O glass.

On the other hand, an empirical rule for the multiphonon relaxation rate is written as

$$W_{mp} = W_0 \exp(-\alpha \Delta E), \quad (5)$$

where  $W_0$  is a positive constant depending on host glasses,  $\Delta E$  is an energy gap between the excited state energy level of interest and immediately lower level [18]. It can be seen from (5) that the multiphonon relaxation rate is exponentially increased with decreasing  $\Delta E$ . And  $\alpha$  is given by

$$\alpha = \frac{1}{h\nu} \left[ \ln \left( \frac{p}{g} \right) - 1 \right], \quad (6)$$

where  $h\nu$  is the phonon energy coupled to rare earth ions,  $p$  is the effective number of phonons participating in the multiphonon relaxation and  $g$  is electron-phonon coupling strength [19]. Therefore, it is considered from the above (5) and (6) that the multiphonon relaxation rate is increased and the measured lifetime is decreased by increasing the phonon energy of host glasses.

B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and GeO<sub>2</sub> are glass network formers having phonon energy higher than that of TeO<sub>2</sub>. The addition of these formers into tellurite glasses increases the phonon energy of host glasses. The energy gap between <sup>4</sup>I<sub>11/2</sub> and <sup>4</sup>I<sub>13/2</sub> is about 3600 cm<sup>-1</sup>. The highest phonon energy of borate glass, germanate glass, and tellurite glass is approximately 1400 cm<sup>-1</sup>, 900

Table 3. Calculated radiative transition rates ( $W_r$ ), measured lifetimes ( $\tau_m$ ), quantum efficiencies ( $\eta$ ), and multiphonon relaxation rates ( $W_{mp}$ ) of  $Er^{3+}$  in tellurite glasses.

glass	transition	$W_r$ ( $s^{-1}$ )	$\tau_m$ ( $\mu s$ )	$\eta$ (%)	$W_{mp}$ ( $s^{-1}$ )
1	$^4I_{13/2} \rightarrow ^4I_{15/2}$	246	4200	103	0
	$^4I_{11/2} \rightarrow ^4I_{13/2}, ^4I_{15/2}$	306	190	6	4960
2	$^4I_{13/2} \rightarrow ^4I_{15/2}$	235	3600	85	42
	$^4I_{11/2} \rightarrow ^4I_{13/2}, ^4I_{15/2}$	295	40	1	24700
3	$^4I_{13/2} \rightarrow ^4I_{15/2}$	231	4500	104	0
	$^4I_{11/2} \rightarrow ^4I_{13/2}, ^4I_{15/2}$	289	160	5	5960
4	$^4I_{13/2} \rightarrow ^4I_{15/2}$	233	4100	96	11
	$^4I_{11/2} \rightarrow ^4I_{13/2}, ^4I_{15/2}$	292	55	2	17900

\* The composition of the glass 1 is  $75TeO_2-20ZnO-5K_2O$ , the glass 2  $60TeO_2-15BO_{3/2}-20ZnO-5K_2O$ , the glass 3  $60TeO_2-15GeO_2-20ZnO-5K_2O$ , and the glass 4  $60TeO_2-7.5GeO_2-7.5BO_{3/2}-20ZnO-5K_2O$ .

Table 4.  $\sigma_a$ ,  $\sigma_e$  and  $\sigma_e \times \tau_m$  for the  $Er^{3+}$ :  $^4I_{13/2} \rightarrow ^4I_{15/2}$  transition in the tellurite glasses at peak wavelength.

Composition	$\sigma_a$ (peak $\lambda$ )	$\sigma_e$ (peak $\lambda$ )	$\sigma_e \times \tau_m$
$75TeO_2-20ZnO-5K_2O$	$8.55 \times 10^{-21} cm^2$ (1530nm)	$8.82 \times 10^{-21} cm^2$ (1530nm)	$3.70 \times 10^{-23} cm^2 s$
$60TeO_2-15BO_{3/2}-20ZnO-5K_2O$	$7.39 \times 10^{-21} cm^2$ (1534nm)	$7.82 \times 10^{-21} cm^2$ (1535nm)	$2.82 \times 10^{-23} cm^2 s$
$60TeO_2-15GeO_2-20ZnO-5K_2O$	$7.38 \times 10^{-21} cm^2$ (1536nm)	$7.95 \times 10^{-21} cm^2$ (1537nm)	$3.58 \times 10^{-23} cm^2 s$
$60TeO_2-7.5GeO_2-7.5BO_{3/2}-20ZnO-5K_2O$	$7.38 \times 10^{-21} cm^2$ (1534nm)	$7.84 \times 10^{-21} cm^2$ (1535nm)	$3.18 \times 10^{-23} cm^2 s$

$cm^{-1}$ , and  $700 cm^{-1}$ , respectively [6]. Only 2~3 phonons need to be combined in borate glasses in order to bridge the energy gap between  $^4I_{11/2}$  and  $^4I_{13/2}$ , while approximately 4 and 5 phonons need in germanate glasses and tellurite glasses, respectively. Thus, only in the case of the  $B_2O_3$  substitution into tellurite glasses did the  $W_{mp}$  of the  $^4I_{11/2} \rightarrow ^4I_{13/2}$  transition increase. On the other hand, the energy gap between  $^4I_{13/2}$  and  $^4I_{15/2}$  is about  $6500 cm^{-1}$ , and thus the multiphonon relaxation rate is very small. The lifetime of the  $^4I_{13/2}$  level is hardly affected by the change of the phonon energy in host glasses. Therefore, the decreasing effect on the  $^4I_{13/2}$  lifetime by the  $B_2O_3$  substitution was small. In the case of the  $GeO_2$  substitution, the measured lifetime of the  $^4I_{13/2}$  level increased. This is considered to result from the increase of intrinsic radiative lifetime ( $\tau_r = 1/W_r$ ) with the  $GeO_2$  substitution as shown in Table 3. The intrinsic radiative lifetime is increased by lowering the refractive indices [20], and the  $GeO_2$  substitution reduced the refractive indices as shown in Table 2.

The peak wavelength of the emission cross-section for the  $^4I_{13/2} \rightarrow ^4I_{15/2}$  transition was shifted to a long wavelength side by the  $B_2O_3$  and  $GeO_2$  substitutions as shown in Table 4. The

spectral gain profile of EDFA strongly depends on the difference spectrum of  $\sigma_e - \sigma_a$  [20]. The peak wavelength of  $\sigma_e - \sigma_a$  was also shifted to a long wavelength side by the  $B_2O_3$  and  $GeO_2$  substitution as shown in Fig. 5. Thus, the corresponding spectral gain profile is expected to shift to a long wavelength region.

The fluorescence efficiency of an active ion in solids can be expressed in terms of a combination of various spectroscopic parameters such as absorption and emission cross-sections, excited state lifetimes, transition probabilities, and concentration of dopant ions [21]. The large emission cross-section and the long lifetime of the excited state energy level make the rare earth doped materials promising materials for fiber amplifier applications [22], [23]. The absorption and emission cross-sections of  $Er^{3+}$ :  $^4I_{13/2} - ^4I_{15/2}$  in  $75TeO_2-20ZnO-5K_2O$  and  $60TeO_2-7.5GeO_2-7.5BO_{3/2}-20ZnO-5K_2O$  glasses are also shown in Fig. 5. The absorption cross-sections were determined from absorption spectrum, and the emission cross-sections were calculated by McCumber theory [24]. According to McCumber theory, the emission cross-sections and the absorption cross-sections are related by

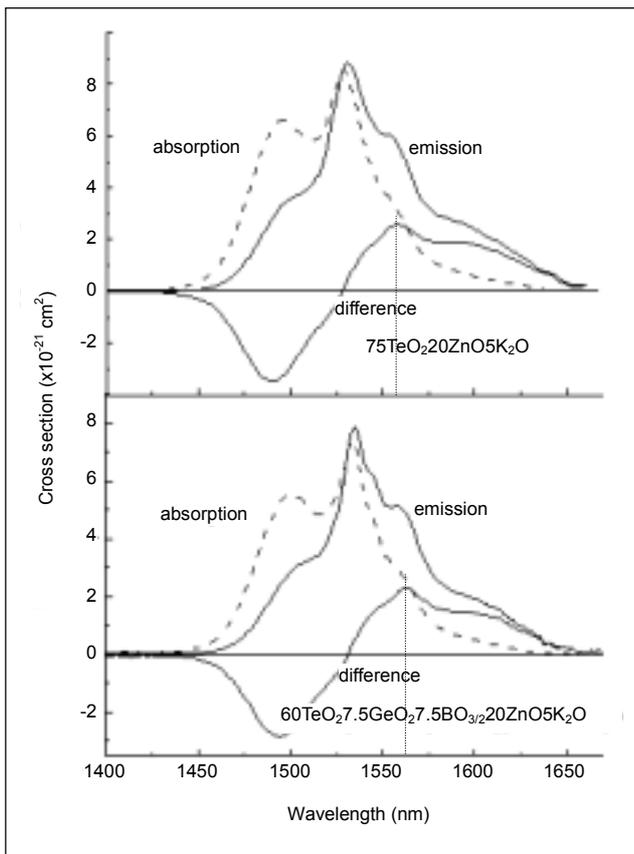


Fig. 5. The spectra of absorption cross-section ( $\sigma_a$ ), emission cross-section ( $\sigma_e$ ), and  $\sigma_e - \sigma_a$  for the  $\text{Er}^{3+}: {}^4I_{13/2} \rightarrow {}^4I_{15/2}$  transition in the tellurite glasses.

$$\sigma_e(\nu) = \sigma_a(\nu) \exp[(\varepsilon - h\nu)/kT], \quad (7)$$

where  $\varepsilon$  is the temperature dependent excitation energy,  $h$  is the Plank constant,  $k$  is the Boltzmann constant, and  $T$  is the temperature. The value of  $\varepsilon$  was determined by using the procedure provided in [25]. The emission cross-sections decreased with the  $\text{B}_2\text{O}_3$  and  $\text{GeO}_2$  substitutions for  $\text{TeO}_2$  as shown in Table 4. The decreasing effect on the emission cross-section by the  $\text{GeO}_2$  substitution was smaller than that by the  $\text{B}_2\text{O}_3$  substitution. The  $\text{B}_2\text{O}_3$  and  $\text{GeO}_2$  substitutions for  $\text{TeO}_2$  also lowered refractive indices of host glasses. The emission cross-section is expected to be decreased with lowering the refractive index of a host glass, because the stimulated emission cross-section owing to the electric dipole-moment transition of rare earth ions is increased as the refractive index of a host glass is raised [ $\sigma \sim (n^2+2)^2/n$ ] [26]. Often the value of  $\sigma_e$  (emission cross-section)  $\times \tau_m$  (measured lifetime) is used as a material parameter of estimation for fiber amplifier applications [27], [28]. The value of  $\sigma_e \times \tau_m$  for the  $\text{Er}^{3+}: {}^4I_{13/2} \rightarrow {}^4I_{15/2}$  transition in the  $60\text{TeO}_2\text{-}15\text{BO}_3\text{-}20\text{ZnO-}5\text{K}_2\text{O}$  glass was reduced by about 24% compared to that in the  $75\text{TeO}_2\text{-}20\text{ZnO-}5\text{K}_2\text{O}$  glass, while that of

the  $60\text{TeO}_2\text{-}15\text{GeO}_2\text{-}20\text{ZnO-}5\text{K}_2\text{O}$  glass was reduced merely by 3%. The  $\text{GeO}_2$  substitution reduced the emission cross-section, but extended the lifetime. Thus, the  $\text{GeO}_2$  substitution scarcely changed the value of  $\sigma_e \times \tau_m$  in  $\text{Er}^{3+}$ -doped tellurite glasses. However, only the  $\text{GeO}_2$  substitution was not enough to raise the multiphonon relaxation rate of  ${}^4I_{11/2} \rightarrow {}^4I_{13/2}$  transition as shown in Table 3. Therefore,  $\text{TeO}_2\text{-GeO}_2\text{-B}_2\text{O}_3\text{-MO-R}_2\text{O}$  glass system is expected to be a suitable host glass for the tellurite-based erbium-doped fiber amplifier material with a high 980 nm pump efficiency, where M indicates a divalent metal such as Zn and Ba and R indicates an alkali metal.

#### IV. CONCLUSIONS

The substitutions of  $\text{B}_2\text{O}_3$  and  $\text{GeO}_2$  improved the thermal stability of tellurite glasses. The substitution of  $\text{B}_2\text{O}_3$  into tellurite glasses significantly raised the multiphonon relaxation rate of  $\text{Er}^{3+}: {}^4I_{11/2} \rightarrow {}^4I_{13/2}$ , which was thus expected to enhance the 980 nm pumping efficiency in T-EDFA. However, the  $\text{B}_2\text{O}_3$  substitution caused the reduction of the  ${}^4I_{13/2}$  lifetime and the emission cross-section for  $\text{Er}^{3+}: {}^4I_{13/2} \rightarrow {}^4I_{15/2}$ . On the other hand, the  $\text{GeO}_2$  substitution into the tellurite glasses extended the  ${}^4I_{13/2}$  lifetime and slightly reduced the emission cross-section, but the increasing effect on the multiphonon relaxation rate for the  ${}^4I_{11/2} \rightarrow {}^4I_{13/2}$  transition was small. Therefore,  $\text{TeO}_2\text{-GeO}_2\text{-B}_2\text{O}_3\text{-MO-R}_2\text{O}$  glass system is expected to be a suitable host glass for the tellurite-based erbium-doped fiber amplifier material with a high 980 nm pump efficiency.

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